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PROCEEDINGS
# of the
1968 Conference
on
Citrus Chemistry
and Utilization

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held at
Winter Haven, Fla.
October 11, 1968

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Agricultural Research Service
United States Department of Agriculture

PREFACE

The Conferences on Citrus Chemistry and Utilization are sponsored by the Southern Utilization Research and Development Division of USDA's Agricultural Research Service to report research developments in the broad area of processing, marketing, and utilization, and to provide for exchange of information that will benefit the industry and future research.

This report summarizes the statements of the various speakers during the Conference, and gives an account of the discussions that followed. If further details are desired regarding any subject presented here, they may be obtained by communicating with the author concerned.

IN RECOGNITION: At this Conference, recognition was made of the many services to the citrus industry by L. G. MacDowell as he retires as Scientific Research Director for the Florida Citrus Commission. Dr. MacDowell has given generously of his talents as Research Director. Special note is taken of the extensive and effective cooperation with the U.S. Department of Agriculture and especially with the Citrus Products Station and its successor, the Fruit and Vegetable Products Laboratory at Winter Haven.

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PROCEEDINGS OF THE 1968 CONFERENCE ON CITRUS CHEMISTRY AND UTILIZATION
HELD AT WINTER HAVEN, FLA., OCTOBER 11, 1968

M. J. Copley, General Chairman

Dr. Copley, General Chairman, called the conference to order and introduced M. K. Veldhuis who, on behalf of the Agricultural Research Service, welcomed those in attendance.

SESSION I: C. H. (Harry) Neufeld, Chairman

OXIDATION OF ALCOHOLS, ALDEHYDES, AND PHENOLS BY ENZYME PREPARATIONS FROM CITRUS JUICE

by

J. H. Bruemmer and B. Roe
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by J. H. Bruemmer)

The primary alcohols in the homologous series from methanol to decanol, except heptanol, have been found in orange essence. None of them noticeably possesses the characteristic flavor and aroma of orange so that their major contribution to essence is probably in the fruit as precursors for aldehydes and other flavor compounds. To understand this precursor function of the alcohols with the view towards its control, the oxidation of alcohols and aldehydes by enzyme preparations from orange juice was examined. The role of phenol oxidation in maintaining the redox state of the coenzymes in these reactions was also examined.

Most of the known enzyme reactions involving the oxidation of primary alcohols are bimolecular with the coenzyme, nicotinamide-adenine dinucleotide (NAD). Therefore, the principal reaction studied has been:

$$\text{Alcohol} + \text{NAD} \xleftrightarrow[\text{dehydrogenose}]{\text{Alcohol}} \text{aldehyde} + \text{NADH}_2$$

The rate of reaction for each alcohol and aldehyde was measured by following the formation or disappearance of NADH_2 spectrophotometrically at 340 mμ. Solubility of the higher molecular weight compounds was aided by the addition of Tween 80.

The enzyme preparations were separated from neutralized orange juice by salt precipitation. In some cases they were purified further by dialysis and by differential absorption on cellulose ion exchange columns.

Table 1 lists the oxidation rate for an orange juice enzyme preparation with 10 alcohols relative to the rate with ethanol. Little or no oxidation was obtained with C-7 to C-10 alcohols.

This same enzyme preparation catalyzed the reverse reaction. The relative reduction rates shown in table 2 indicate that acetaldehyde, butanal, hexanal, and octanal are the preferred substrates. These four aldehydes are present in orange essence; pro-

Table 1.—NAD-specific alcohol dehydrogenase activity

Alcohol	$\text{Alcohol} + \text{NAD} \xrightarrow{\text{pH } 9.6} \text{aldehyde} + \text{NADH}_2$ Relation oxidation rate
Methanol	0
Ethanol	1.0
Propanol	0.24
Butanol	0.22
Pentanol	0.20
Hexanol	0.18
Heptanol	0.03
Octanol	0.02
Nonanol	0
Decanol	0

Table 2.—NAD-specific aldehyde reductase activity

$$\text{Aldehyde} + \text{NADH} \xrightarrow{\text{pH } 6.5} \text{Alcohol} + \text{NAD}$$

Aldehyde	Relative reduction rate	Reduction-oxidation rate
Acetaldehyde+	1.0	5
Propanal	0.15	3.6
Butanal	0.48	13
Pentanal	0.18	5.4
Hexanal	0.48	16.5
Heptanal	0.15	30
Octanal	0.32	89
Decanal	0.11	0 o

Table 3.—Phenols oxidized by orange enzyme preparations

O-OR p-Diphenols	O-Methoxy-phenols
Catechol	Ferulic acid
Quinol	Feruloyl putrescine
Ubiquinol	Hesperetin
O-dihydroxyphenylalanine	
Chlorogenic acid	
Catechin	
Quercetin	
Quercetrin	
Rutin	
Eriodictyol	

panal, pentanal, and heptanal have not been detected in essence. This reverse reaction with the aldehydes is faster than the forward reaction. The ratios of the absolute reduction-oxidation rates shown in table 2 increase in the series from acetaldehyde to octanal.

This demonstration that orange-essence alcohols can be reversibly oxidized by enzyme preparations from the fruit suggests that similar reactions probably occur in vivo. Furthermore, if these are the major reactions for the alcohols and aldehydes in the fruit, then their steady-state concentration will be greatly influenced by these reactions.

The oxidation of aldehydes by orange juice-enzyme preparations does not follow the pattern described for alcohol oxidation. Glyceraldehydephosphate is oxidized by the enzyme preparation in a NAD-specific bimolecular reaction but acetaldehyde does not participate in this reaction. Acetaldehyde reacts with the indicator 2,6-dichlorophenol in the presence of the enzyme preparation, however. This redox indicator gives a measure of the reaction rate. Hexanal, octanal, and decanal do not replace acetaldehyde in this reaction.

The aldehydes and acids may be enzymically interrelated through some derivative. Very active phosphatase activity has been observed in orange juice preparations. This may have hydrolyzed phosphorylated derivatives to inactive free forms.

Also investigated was the role of phenols as intermediates in the reoxidation of $NADH_2$ to NAD. The ratio of $NADH_2$ to NAD affects the rates of alcohol oxidation and of aldehyde reduction by alcohol dehydrogenase. Therefore, to control reactions forming alcohols or aldehydes, the redox ratio of NADH to NAD must be controlled.

Table 3 lists the ortho- and para-diphenols that are oxidized by purified enzyme preparations from orange juice. Several of these diphenols and methoxy phenols are present in orange juice. The paraquinone, formed by the oxidation of p-quinol can function as the oxidant in the enzymic reoxidation of $NADH_2$ to NAD. The sequence of reactions for the oxidation of $NADH_2$ by O_2 through quinone is as follows:

$$\text{p-quinone} + NADH_2 \longrightarrow \text{p-quinol} + NAD \quad (1)$$

$$\text{p-quinol} + \tfrac{1}{2}O_2 \longrightarrow \text{p-quinone} + H_2O \quad (2)$$

$$\text{Total} \quad NADH_2 + \tfrac{1}{2}O_2 \longrightarrow NAD + H_2O$$

Both reactions (1) and (2) have been demonstrated with enzyme preparations from orange vesicles.

Thus, orange juice contains enzymes that can effect the reversible oxidation of alcohols to aldehydes. The coenzymes reduced in these reactions can be reoxidized with O_2 through the intermediacy of p-quinones. These reactions may be significant in the synthesis of flavor compounds such as aldehydes from alcohols in the fruit. However, conventionally squeezed orange juice does not support these reactions. These enzymes would not be expected to affect flavor of processed and stored juice except through their influence on fruit from which the products are derived.

DISCUSSION

Question: Can this relationship between the coenzyme redox state and alcohol formation be applied to whole fruit?

Dr. Bruemmer: Yes! It should be possible to treat whole fruit to bring about an increase in the alcohol concentrations. For example, anaerobiosis or O_2—transport inhibition should suppress the normal coenzyme reoxidation system. Under these conditions the ratio of the reduced to the oxidized coenzyme would increase. The alcohol-aldehyde system would respond to the increase in the redox ratio, resulting in the reduction of aldehydes to alcohols. The phenol-quinone enzyme system and other oxidation-reduction system would probably also respond to the redox ratio with a general shifting from the oxidized to the reduced form of the substrates.

THE COMPOSITION OF THE "CARBONYL" FRACTION OF VALENCIA ORANGE PEEL OIL

by

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U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by E. D. Lund)

The isolation and identification of the flavor components contained in the volatile part of the orange peel oil has been a subject of considerable research by the Fruit and Vegetable Products Laboratory as well as others. Since most of the orange flavor can be found in this volatile fraction of the peel oil, research on the composition of this fraction is considered important as a basis for eventual formulation of orange flavor in terms of a group of compounds isolated from orange and possessing the basic orange flavor.

The "carbonyl" fraction represents the last remaining unidentified group of compounds in the volatile portion of Valencia orange oil, the hydrocarbon and alcohol fractions having been dealt with in earlier publications. The seventeen aldehydes and ketones and three esters contained in this fraction are listed below:

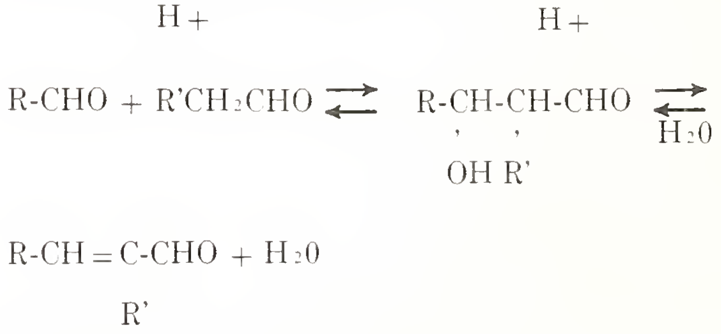
"Carbonyl" Components of Valencia Orange Oil

1. n-hexanal
2. n-heptanal
3. n-octanal
4. 6-methyl-5-hepten-2-one
5. *n-nonanal*
6. trans-limonene oxide
7. cis-limonene oxide
8. octyl acetate[1]
9. *citronellal*
10. *n-decanal*
11. n-undecanal
12. neral[1]
13. geranial[1]
14. n-dodecanal
15. *carvone*
16. perillyl acetate[1]
17. perillyl aldehyde
18. 1, 8-p-menthadiene-9-yl acetate[1]
19. piperitenone
20. aldehyde A
21. *nootkatone*
22. *β-sinensal*
23. aldehyde B
24. *α-sinensal*
25. aldehyde C
26. aldehyde D
27. aldehyde E

The underlined compounds represent the most abundant constituents as estimated from the relative size of the peaks in the gas-liquid chromatogram. All of these abundant constituents have potent and distinctive odors which probably contribute significantly to the characteristic orange aroma. The saturated aliphatic aldehydes contribute a sweet pungent fatty odor: neral, geranial, and citronellal a pungent citruslike odor, carvone a minty odor, nootkatone the odor of grapefruit, and the sinensals a sweet pungent penetrating odor.

Trans-and *cis*-limonene oxide have never been reported as constituents of cold-pressed orange oil although not carbonyl containing compounds, they were included because they are found in one of the fractions along with the carbonyl compounds. A number of the alcohols in orange oil are related to limonene oxide and are vossibly formed by acid-catalyzed ring opening of the oxides.

Aldehydes A-E represent a series of α, β-unsaturated aldehydes with the general formula R-CH = C-CHO where R and R' are saturated straight-chain hydrocarbon radicals, $CH_3(CH_2)n$ - with n = 5,6,7, or 8. These aldehydes are formally related to the straight chain saturated aldehydes present in relatively large quantities in orange oil, octanal, nonanal, and decanal, by acid-catalyzed aldol condensation according to the following set of equilibria:



$$\text{R-CHO} + \text{R'CH}_2\text{CHO} \overset{H+}{\rightleftharpoons} \text{R-}\underset{\text{OH}}{\text{CH}}\text{-}\underset{\text{R'}}{\text{CH}}\text{-CHO} \underset{H_2O}{\overset{H+}{\rightleftharpoons}} \text{R-CH}=\underset{\text{R'}}{\text{C}}\text{-CHO} + H_2O$$

Whether or not such an equilibrium exists and the extent to which it influences the flavor of natural orange products has not been established. The α, β-unsaturated aldehydes themselves contribute little to the flavor other than a faint, burnt fatty quality.

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[1] **Isolated and identified as a component of Valencia orange peel oil for the first time.**

THE CHEMISTRY OF DELAYED BITTERNESS IN CITRUS JUICES

by

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Certain citrus juices (early-season to midseason Washington Naval, Shamouti, and Australian Valencia oranges) gradually become bitter on standing or during processing, whereas, the fruit when eaten fresh or the juice immediately after preparation are not bitter. This phenomenon, which was noted many years ago, is generally referred to as delayed bitterness.[1] The bitter principle of processed naval orange juice is the triterpenoil dilactone called limonin (fig. 1). The presence of limonin in bitter naval orange juice was reported (3) even before the complete structure of the compound was known (1). Subsequent work has confirmed that limonin is the only limonoid present in bitter naval orange juice (2, 8) and that limonin also is found in grapefruit juice (9) under certain conditions in Valencia orange juice (6), and Shamouti orange juice (13). However, the reason for the delayed development of bitterness in citrus juices has remained unresolved over the years.

Recent research carried out in our laboratory has led to an explanation of the delayed bitterness phenomenon (7). This paper presents a summary of the results of that research. The individual publications which contain the original reports of various phases of this work are cited throughout this paper and may be consulted for experimental details and further discussion.

Our research has shown that, whereas, the bitter compound limonin occurs in naval orange juice after the juice becomes bitter, it does not occur in the tissues of the healthy, intact fresh fruit to any significant extent. Rather, a close relative of limonin which is a nonbitter compound; namely, limonoate A-ring (fig. 2) (a new compound) is found (8, 12). This compound differs from limonin in that in aqueous solutions it is nonbitter at 50 p.p.m., whereas, limonin is detectably bitter at 2 to 7 p.p.m. and extremely

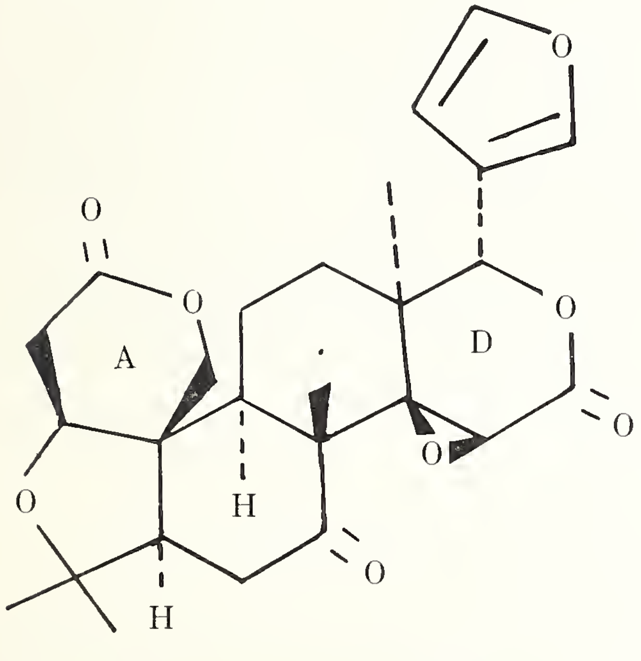

Figure 1.—Structure of limonin (bitter).

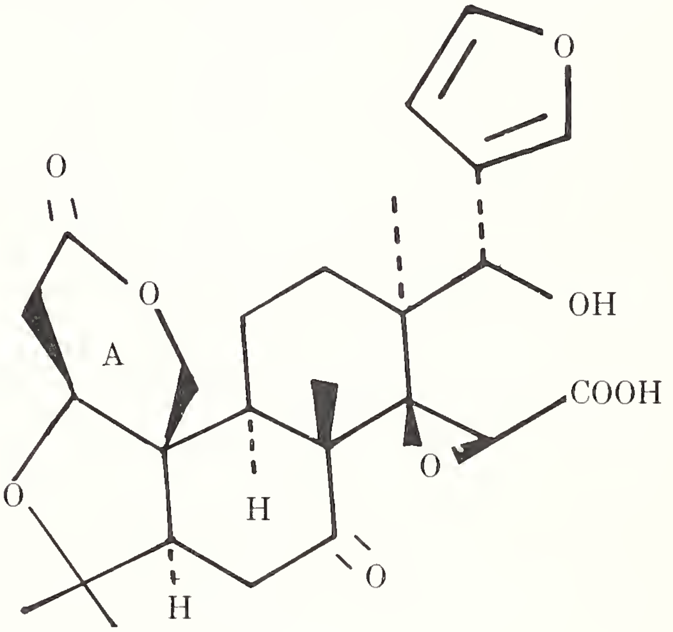

Figure 2.—Structure of limonoate A-ring lactone (nonbitter) the free acid.

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[1] The delayed bitterness of orange juice should not be confused with the bitterness of grapefruit and the Seville orange. Both of these fruits are bitter when eaten fresh as well as made into juice. The compounds responsible for the bitterness of fresh grapefruit and Seville orange are flavanone neohesperidosides (5).

bitter at 15 to 20 p.p.m. Limonoate A-ring lactone was found to occur in the structural tissues of the endocarp and in the albedo of the peel of naval oranges and grapefruit. In addition, the limonoate A-ring lactone was found to be readily converted into limonin in solutions having the same acidity as orange juice. Therefore, in juice manufacture when the broken tissues of the fruit mix with the acidic juice, the nonbitter limonoate A-ring lactone, which is unstable under these conditions, is converted into the bitter compound limonin and the juice gradually becomes bitter. If the juice is heated, the rate of conversion of the nonbitter compound into limonin is increased and the juice becomes bitter more rapidly.

Higby (4) reported that bitterness of naval orange juice could be minimized by avoiding tissue maceration and by immediately separating the coarser tissue fraction from the extracted juice. The chemical basis of this process is now clear. Avoiding maceration retards extraction of limonoate A-ring lactone into the liquid phase and at the same time facilitates removal of this potential source of bitterness before limonin is formed. It is hoped that these new findings will both aid and stimulate the commercial application of this process.

During the work on the identification of the limonoate A-ring lactone (11), we discovered an enzyme in fruit tissue extracts which catalyzes the conversion of limonoate A-ring lactone to limonin in acidic solutions. This enzyme appears to be responsible for the traces of limonin occasionally encountered when extracting limonoate A-ring lactone from the fruit tissues. It may be partly responsible for the conversion of limonoate A-ring lactone into limonin in orange and grapefruit juices during commercial juice preparation. We have subsequently isolated and purified the enzyme and studied its properties (10).

Another well known but unexplained aspect of the delayed bitterness phenomenon is the fact that at varying times after commercial maturity is reached (depending on the year) naval oranges will produce juice that does not become bitter after standing or processing. In a study of naval oranges at different stages of maturity (8), we found that limonoate A-ring lactone gradually disappears from the tissues as the fruit ripens beyond commercial maturity and that the limonin content of the juice made from these fruits follows a parallel course. Thus, the juice made from naval oranges whose tissues contain no limonoate A-ring lactone contains no limonin and is nonbitter.

On the basis of these studies, it can be concluded that limonin does not occur to any significant extent in the tissues of intact, healthy oranges or grapefruit, although it is a natural constituent of citrus seeds. Rather limonoate A-ring lactone, a nonbitter compound, is present in these tissues. On the other hand, limonin may be found as a constituent of intact fruits in instances where the fruit has been damaged and the acids and enzymes released from the damaged tissues have brought about conversion of the limonoate A-ring lactone into limonin. This is probably the reason for the bitterness occasionally observed where oranges have been damaged by frost before reaching commercial maturity.

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DISCUSSION

Question: I was under the impression delayed bitterness reaction took place in heated juice. How would enzymes fit in this picture?

Dr. Maier: Acid alone converts the precursor to limonin and heat helps it along. You do not need the enzyme.

Question: Was the enzyme you identified isolated from tissues or juice?
Dr. Maier: The tissues. We haven't tried the juice. However, the enzyme is soluble.

Question: Has any work been done on effect of rootstock?
Dr. Maier: Yes. Kefford in Australia found budding Valencia on sweet orange stock resulted in considerably less bitterness.

Question: Have you tested lime juice?
Dr. Maier: No. Is it bitter immediately after extraction or does it develop on standing? It could well be limonin. Limonin appears to be ubiquitous in citrus. Probably if Valencias were harvested too early their juice would turn bitter.

Question: Have any observations been made as to weather, soil, or fertilizer and their effects on limonin?
Dr. Maier: There have been some. A principal difficulty has been lack of a good analytical method. Also, the nature of the problem was not really known. The same strains of Valencia grown in the United States and in Australia generally exhibit bitterness only "down-under."

DIFFERENTIAL FATTY ACIDS STUDIES OF SEEDS AND JUICE FROM SEVERAL CITRUS SPECIES

by

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U. S. Fruit and Vegetable Products Laboratory
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(Presented by S. Nagy)

Lipid oxidation has been implicated as one of the causative factors in flavor deterioration of processed juice. Available information in other food product areas indicates that oxidation of unsaturated fatty acids, especially the highly unsaturated acids, is a contributing factor to off-flavor development. To further understand the role of lipids in flavor deterioration, we have undertaken a preliminary study of the fatty acid composition in seeds and juice from several citrus species.

Juice and seed fatty acid methyl esters were identified by employing several criteria, namely, (a) comparison of retention time to those for standards, (b) separation of fatty acids on silver nitrate impregnated thin-layer plates according to the degree of unsaturation, (c) hydrogenation of methyl esters to yield saturated carbon skeletons, and (d) plots of log retention time versus carbon number from data derived from nonpolar (OV101) and polar (DEGS) columns to yield information on effective chain lengths.

Table 1.—Major fatty acids of citrus juices (mole percent)

Fatty acid	Orange	Grapefruit	Lemon	Lime	Tangerine
16:0	19.4	21.5	22.9	20.8	19.6
16:1	4.6	3.9	1.0	4.0	4.5
18:0	0.7	1.2	3.1	2.2	1.0
18:1	25.7	21.0	7.0	15.6	33.3
18:2	31.6	36.2	41.2	32.9	25.4
18:3	7.8	10.7	17.0	17.3	11.9
22:0	0.3	0.2	0.6	0.4	0.3
24:0	0.7	0.7	1.4	1.3	0.6
26:0	0.5	0.4	0.7	0.8	T

No. of carbon atoms: Number of double bonds.

Table 2.—Major fatty acids of citrus seeds (mole percent)

Fatty acid	Orange	Duncan grapefruit	Marsh grapefruit	Lemon	
16:0	27.8	28.8	29.5	20.4	22.5
16:1	0.9	0.7	0.5	0.5	0.5
18:0	4.9	3.0	2.5	3.1	4.5
18:1	26.0	20.9	20.1	26.3	22.7
18:2	37.1	42.2	41.7	38.0	45.3
18:3	3.2	4.0	4.9	11.1	4.0

Fatty acids were analyzed in juices from Persian lime, Valencia orange, Marsh grapefruit, Eureka lemon, and tangerine. Seed fatty acids were examined in Valencia orange, Marsh and Duncan grapefruit, Eureka lemon, and tangerine. The major fatty acids detected in juice and seeds are shown in tables 1 and 2, respectively. These acids taken collectively comprise greater than 95 percent of all acids in juice and greater than 99 percent in seeds.

The vast majority of seed acids belong to the even carbon series with chain lengths of 16 and 18 carbon atoms predominating. Acids with even carbon lengths below 16 and above 18 are found in trace amounts. Heptadecanoic acid was the only odd carbon acid to be detected in trace amounts. The fatty acid composition of juice is extremely complex and manifests numerous trace acids. While the even carbon series dominates, odd carbon acids from C_{15} to C_{25} have been detected in trace amounts. The presence of branched-chain acids has also been detected in trace quantities.

* * *

SYNTHETIC SWEETENERS FROM CITRUS BYPRODUCTS

by

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Southeastern Utilization Research and Development Division
Athens, Ga.

(Presented by W. F. Talburt)

The consumption of noncaloric sweeteners has increased rapidly in the past 5 or 6 years. This expansion is likely to continue. The most important factor supporting this conclusion is the expected growth in sales of soft drinks and the proportion of these products that is likely to be made with noncaloric sweeteners.

At the present time, cyclamate and saccharin are the only two important noncaloric sweeteners in use throughout the world. In 1965, the U.S. production of cyclamate was 10.3 million pounds, and saccharin was 2.6 million pounds. Together they had a value of $11.7 million. It is estimated that by 1970, U.S. consumption will be about 21 million pounds of cyclamate and 4 million pounds of saccharin.

The dihydrochalcones are characterized by their pleasant sweetness and no bitter aftertaste. The onset of sweetness is relatively slow but it is long lasting. By combining these substances with cyclamate, it appears that a taste profile, very much like that of sucrose, can be obtained. The long lasting sweetness of the dihydrochalcones might make them useful also in a number of products in which noncaloric sweeteners have not been used in the past, such as, chewing gums, medicated troches, or mouth washes.

If one-half (in terms of sweetening power) of cyclamate and of saccharin were to be replaced by naringin dihydrochalcone or hesperidin glucoside dihydrochalcone, it would represent an annual market for about 6.1 million pounds by 1970. Currently hesperidin and naringin sell for around $8 per pound; but if a large demand for them were to develop, the price might well drop to $1 per pound. Since about 1.5 pounds of the citrus flavanones would be required to make 1 pound of dihydrochalcones, this would represent sales of about $9 million per year for the citrus industry by 1970. In addition, chemical manufacturers who convert the flavanones to dihydrochalcones would have sales of $11 million worth of the finished product.

Some of the procedures and problems of converting the starting materials to the final products will be discussed.

DISCUSSION

Question: Does your agency expect to work on official acceptance of the dihydrochalcone sweetener?

Dr. Copley: We have not made any decisions yet. We prefer to see if any actual uses develop.

(A discussion followed on the high cost of establishing the safety of the product: high dosages on many large animals for extended periods of time.)

Question: Does your chart showing increased usage of sweeteners indicate a per capita increase, or is it just a population increase?

Mr. Talburt: The data showed a population increase of 26 percent, with a total increase in sweetener consumption of 36 percent. This indicates an increase in per capita usage.

Question: Our information differs from yours. The total use of sweeteners is increasing, but the per capita use has decreased.

Mr. Talburt: Our data are taken from a USDA release.

Question: Are sufficient quantities of dihydrochalcone sweetener available to carry out the extensive feeding tests previously mentioned?

Mr. Talburt: They are not at hand but the method of preparation is simple.

Question: Has USDA taken a hard look at the recent review of the safety of cyclamates and saccharin with a view of replacing them with dihydrochalcones?

Mr. Talburt: Prediction of the future of artificial sweeteners would be hazardous at this particular time. Perhaps Dr. Beck would like to speak on the question.

(Karl Beck of Abbott Laboratories, Chicago, Ill., proceeded with quite a detailed discussion of reported tests that led toward review by the Food and Drug Administration of the safety of cyclamates and saccharin, and then described the extensive tests that are underway to settle the question. He did not believe that the present commercial sweeteners currently used will lose out, but that the dihydrochalcones may absorb some of the predicted increases in the use of artificial sweeteners.)

SESSION II: M. W. Ratcliff, Chairman

STUDIES ON HYDROXYMETHYLFURFURAL RELATIONSHIP TO HEAT TREATMENT AND STORAGE IN ORANGE JUICE PRODUCTS

by

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(Presented by P. E. Shaw)

Quality of some processed foods has been related to their hydroxymethylfurfural (HMF) content, because HMF formation parallels off-flavor development in these foods. HMF concentration is an index of the amount of nonenzymic browning undergone by these foods during heat or storage treatment. In honey, for example, determining the HMF content involves dilution with water, treatment with p-toluidine and barbituric acid, and quantitative measurement of absorption at 550 mm. of the pink-colored derivative formed. Even fresh honey collected under the most carefully controlled conditions contains measureable amounts of HMF. In both apple and grape juices, quality can be correlated with HMF content by this method.

Foam-mat dried instant orange juice (IOJ) undergoes a flavor change after storage that has been qualitatively correlated with HMF formation. The results reported below concern our efforts to make a quantitative correlation between HMF content and off-flavor development in IOJ.

The color test that is successful on honey and on single-strength apple and grape juices was not sensitive enough to detect HMF in single strength reconstituted IOJ. Thus, a procedure was developed to concentrate the total HMF from 168 g. of IOJ powder into a small volume suitable for spectrophotometric measurement. The concentration procedure involves:

GENERAL PROCEDURE

a. Making a slurry of 168 g. IOJ and 300 ml. of 1:1 acetone-water.
b. Extracting the slurry with several 300 ml. portion of ether.
c. Concentrating the combined ether extract to small volume under vacuum, adding 10 ml. H_2O and removing the rest of the ether.
d. Filtering the aqueous residue through glass wool.
e. Adjusting the filtrate volume to exactly 10 ml.
f. Preparing a blank from 5 ml. of this filtrate, 12.5 ml. of p-toluidine solution and 2.5 ml. of water.
g. Preparing the colored derivative by treating the other 5 ml. of filtrate with 12.5 ml. of p-toluidine and 2.5 ml. of barbituric acid solution.
h. After 3 to 5 min., measuring the visible absorption of the colored derivative above versus the blank at 550 mm. with a Cary 14 spectrophotometer.
i. Comparing the absorbance with a standard curve prepared from known concentrations of HMF derivative to determine the HMF content.

Reagents: p-Toluidine solution was prepared by dissolving 25 g. of p-toluidine in 125 ml. of isopropanol and 25 ml. of acetic acid, then diluting to 250 ml. with isopropanol. Barbituric acid solution was prepared by dissolving 500 mg. of barbituric acid in 100 ml. of water.

Previous reports noted that maximum color development in this reaction was not reached for 3 to 4 minutes. No mention was made of subsequent color loss with time. Our results showed that considerable

Table 1.—Standard HMF tabulation for known samples.

Five minutes color development	
HMF concentrations	Absorbance values
mg./ml.	
0.0125	0.23
.025	.44
.0375	.60
.050	1.00
.075	1.43

Table 2.—Extraction efficiency for HMF determination in stored IOJ.

Five minutes color development		
Ether extractions	Absorbance values	Amount of HMF
Number		Mg.
6	0.54	0.33
5	.46	.28
4	1.02	.54
3	.33	.19

decrease in absorbance occurred with time. Thus, measurements should be made in 3 to 5 minutes after mixing reagents.

A standard curve was prepared using a series of known concentrations of HMF and the results are given in table 1. Values for absorbance obtained from IOJ samples were compared with a curve prepared from these standard values to obtain the quantity of HMF present.

Samples of IOJ that had been stored at 85° F for 7 weeks, 3 days were analyzed using the procedure described above. The number of ether extractions was varied holding the rest of the procedure constant to determine the smallest number of extractions permitted without appreciable loss of absorbance. The results of this study are presented in table 2. Four extractions with ether seem to be sufficient. Control IOJ that had been at —5° F for the same length of time as the samples in table 2 had no appreciable absorbance.

Conclusions from these results on off-flavor instant orange juice are:

a. Measurable amounts of HMF are formed in stored IOJ when off-flavors have developed.

b. Concentration of the HMF present is required to obtain meaningful results.

c. Preliminary results indicate that correlation of HMF content with off-flavor development is possible.

The applicability of this test for correlating HMF content to degree of heat treatment in canned and chilled single strength orange juice (SSOJ) is being studied. With commercial samples of canned SSOJ there was not enough HMF present to detect in SSOJ without prior concentration. In this case, ether extraction of SSOJ afforded sufficient concentration of the HMF to give measurable quantities. The concentration procedure was as follows:

a. Extracting 46 oz. of juice in a separatory funnel with 4 x 250 ml. of ether.

b. Concentrating the combined ether extract to small volume as was done in step C of the *General Procedure* for IOJ and repeating the remainder of the procedure.

Table 3.—HMF content of stored chilled juice samples [1]

	Absorbance Values		
Time (weeks)	Cold pack glass	Hot pack glass	Hot pack canned
0 (control)	0.02	0.02	0.03
2	.07	.00	.04
6	.07	—	—
7	—	.12	—
9	.08	.08	—

Absorbance values averaged 0.9, and quantities of HMF averaged 0.50 mg. per 46 oz. can of juice. A noteworthy observation here was that the typical odor of canned SSOJ was concentrated in water-insoluble solids trapped by the glass wool plug in step D of the General Procedure. This typical canned juice odor is quite different from the off-flavor of IOJ.

Chilled juice packed under three different sets of conditions was prepared by Dr. Wenzel at the Citrus Experiment Station at Lake Alfred and stored at 85° F for up to 9 weeks. Results of those tests to date are given in table 3.

Conclusions from these studies on canned and chilled SSOJ are:

a. Off-flavor components different from those responsible for off-flavor in IOJ are probably being formed rapidly here.

b. Concentration of these off-flavor components in an ether-soluble, water-insoluble fraction was observed.

c. Studies on the composition of this off-flavor fraction may lead to a test for storage changes in SSOJ.

d. Quantitative HMF test appears of little help in following storage changes in SSOJ because of the small amount formed.

DISCUSSION

Question: What is the difference between your work and that reported years ago by Curl, on furfural in deteriorated canned orange juice?

Dr. Shaw: The furfural content of Instant Orange Juice or of chilled juice is not as great as the HMF content. The p-toluidine derivative of furfural shows an absorption peak at 585 mμ, while that of hydroxymethylfurfural peaks at 550 mμ.

The complete visible spectra of these products exhibit principal peaks very near to 550 mμ. This indicates insufficient furfural to serve as an index of deterioration.

Question: Has any further work been done with the compounds separated by TLC?

Dr. Shaw: No. We were only trying to correlate the HMF test with deterioration of chilled orange juice.

* * *

ORANGE JUICE TABLETS - A NEW CITRUS PRODUCT

by

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(Presented by R. E. Berry)

Previous studies have shown that foam-mat dried citrus juices require densification for improved reconstitution properties. Undensified, ground foam-mat powder was extremely light and fluffy and tended to float and clump when reconstituted. Methods were developed for increasing the bulk density of this powder by passing it through the nip of hard, heavy, steel rolls where pressure was applied forming small, flat, dense flakes. These flakes were then ground to give a powdered material of a much increased bulk density. Studies were undertaken to determine the relationship between densification, changes in bulk density, and the fragility of the densified powder particles.

To study these matters, an experiment was undertaken to form small, flat discs at different pressures, and to determine the amount of shear required to break these discs as an index of fragility. During this experiment, samples were prepared that varied in moisture content from 0.9 to 1.6 percent, and these were subjected to pressures of 3,800 to 19,100 p.s.i. by a ram driven hydraulic press (Carver press). This formed small, firm citrus discs which were then tested in a shear press to determine the amount of shear required to break them. While this experimentation was being carried out, a number of experimentors began eating these discs from time to time and found they were very tasty. This suggested the possibilities of compressing citrus solids into a form like candy for consuming, as opposed to the more traditional idea of dissolving dehydrated citrus solids to reconstitute to juice.

Following this idea which could lead to development of a new product, experiments were planned for producing various types of fruit juice solids in tabletted form for eating. A pilot model tabletting machine was installed with the capability of producing as many as 90 tablets per minute. Punches and dies used with this machine initially were 1/2-inch in diameter. Tablets produced to this time have been about 0.8 grams in weight, ½-inch diameter flat-faced discs, and 3/16-inch thick. Subsequent studies have shown that approximately 3,000 p.s.i. is required on the tablet punch to form these tablets.

Experiments were also conducted to determine what type of tabletting, binding, and releasing agent would be required to make smooth, clean, dust-free tablets which would release easily from the machine. A commercial stearate triglyceride was found effective for this purpose. This is a granular form of a completely edible food product similar to commercial hydrogenated vegetable oils used as shortenings. There are no limits on the safe use of this material in foods. It has been found effective as a tablet binder and release agent in amounts from 1/2 to 2 percent (solids basis). The percent of binder was varied and it was found effective with citrus solids at about 0.25 percent when densified powder was used and about 0.5 percent when undensified powder was used.

These tablets have been prepared from orange-plain, sweetened with sugar and sweetened with cyclamate; grapefruit-plain, sweetened with sugar and sweetened with cyclamate; and a combination referred to as "Citrus Punch" - grapefruit, lime, and strawberry, sweetened with sugar. The process would appear to be applicable to most any other kind of high sugar-containing solids.

A brief study has been made of the manufacturing costs involved in producing these tablets. Basically, if orange solids are about 55 cents per pound (closing prices last season) and foam-mat drying cost run about 8 cents per pound solids, and assuming the loss and additional costs for compressing these solids into tablets is practically negligible, than a pound of citrus solids can be converted to tablets for approximately 65 to 70 cents. This pound of powder will make a substantial number of tablets, the exact number being dependent, of course, upon the size chosen for the tablets. Using tablets of the current size (1/2-diameter) which are equivalent to about 1/4 ounce of orange juice each, over 500 tablets can be prepared from 1 pound of dehydrated juice powder. Of course, even more can be made from this amount of citrus solids when sugar is added. Packaging will add substantially to the cost of production but should not be prohibitive.

Several different types of packaging have been used. They have included foil/poly/paper sealed envelopes, foil/poly envelopes, screw-cap glass jars, and plastic push-cap glass vials. All of these packages have been found suitable. A plain poly pouch was not found suitable. There is some question as to whether cellophane envelopes such as those used for candies of this type might be suitable. They have not been tested to date, but the principal protection required is a moisture barrier.

Studies are presently underway to determine the relative nutritive aspects of these tablets as compared to the original powder, and the original juice from which they were made. Preliminary studies have shown that the ascorbic acid content of these tablets runs about the average value for orange juice.

Considerable interest has been shown in these tablets by pharmaceutical companies as well as different food and candy companies. Most interest is directed toward their potential as camping foods, nutrition supplements, diet foods, and the like. They also offer considerable interest by virtue of affording a means for citrus to compete in a field which has, heretofore, been exclusively the field of synthetic materials.

Attempts have been made to eliminate the natural hydroscopicity of these tablets by coating them. They have been dipped in aqueous solution of methylcellulose and carboxymethylcellulose polymers of different types. They have also been tested with an alcoholic solution of cellulose polymers. Other possibilities which have been tried included dusting with silica or starch. None of these coating methods has met more than a moderate degree of success to date.

A number of materials are being studied as flavor enhancement additives. These include commercial "locked-in" cold-pressed peel oil and several different types of "essence" extracts adsorbed onto dry hydrophilic silica as carrier. These studies are still in progress.

DISCUSSION

Question: How does the quality of OJ Tabs compare with that of IOJ?

Dr. Berry: It is as good as, and perhaps better than, the powder from which it is made. This may be because the tablet dissolves so slowly in the mouth, and there is a much higher concentration of flavor as compared with that of reconstituted powder.

Question: How about the storage stability of the tablets?

Dr. Berry: Storage stability of the tablets is much better. There was no observable change in tablets stored 6 months at 80 ° F. and that is certainly not true with the powder.

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UTILIZATION OF WHOLE GRAPEFRUIT AND ORANGES— A PROGRESS REPORT

by

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(Presented by F. P. Griffiths)

Whole oranges or grapefruit were cooked 5 minutes at 15 p.s.i.g., in a modification of the process of Braverman and Levi[1]. The cooked fruit were comminuted in Chisholm-Ryder screw finisher, using a screen with 0.062-inch openings. The harder parts of the fruit, including scaly parts of the peel, most of the rag, and the seeds, were separated and rejected in this operation; the seeds remained whole. Rejected material from a 90-pound box of oranges was 8-3/16 pounds. The softer portions of the pulped fruit, amounting to approximately 90 percent of the total weight of the starting material, were homogenized in a Manton-Gaulin homogenizer. The homogenized material was canned and stored at -10° F. until utilized. Grapefruit puree was generally debittered with 0.2 percent naringinase (Kumitanase) for 2 hours at 45 to 50° C. before final utilization. Part of the puree was diluted 50 percent with water (2 l. water to 4 l.pulp) and the diluted pulp circulated through a Mojonnier low temperature evaporator at 150 ° F. until the pulp had regained its original volume. A reduction of 30 to 35 percent of the peel oil remaining in the fruit after the cooking operation was achieved.

The homogenized and homogenized-deoiled frozen purees were utilized in the preparation of citrus beverages and nectars of highly acceptable quality. A typical formulation consisted of 100 g. pulp, 125 g. sugar, 25 g. sixfold lemon concentrate and water to 1 l. An orange beverage prepared from this formulation, packed in No. 2 plain cans and No. 303 enameled cans and stored at 70 ° F., has shown no significant deterioration after 150 days, as indicated by taste evaluation ratings.

The pulps have been utilized in citrus-flavored syrups and several other products. Consideration has been given to utilization of the purees in citrus-flavored baked goods.

Another approach to the improved utilization of citrus fruit involves the upgrading of various parts of the fruit now used only for cattle feed. Excess pulp removed from the juice in a finisher subsequent to fruit extraction was utilized along with the puree to obtain a beverage having body similar to hand-extracted juice from whole fresh fruit.

Acceptable syrups have been prepared by ion exchange treatment of citrus peel liquid pressed from the wet peel. Syrups having the best flavors were obtained by passing the liquor through an intermediate strength acid resin (cation form) and followed by treatment in a column of intermediate strength base resin (anion form). The use of lime ($Ca(OH)_2$) in the initial processing of the peel was found to cause, or accentuate, off flavor in the final syrup. By treating the ground peel with 0.3 percent Pectinol at 50° C. for 2 hours, to obtain juice release, instead of lime, this off flavor was avoided. The basic ion exchange resin reduced the naringin content of grapefruit peel liquor tenfold (0.044 to 0.004 percent naringin; 0.031 to 0.0036 percent by Davis Test). From liquors obtained in the first pressings of peel (12 to 15° Brix), syrups of $>$ 60° Brix were obtained by a 10:1 volume concentration (including ion exchange treatment). The extracts obtained by resuspending the expressed peel in water and pressing a second time (3 to 7° Brix) required about a 40-fold concentration to reach $>$ 60 ° Brix. Syrups prepared using the acid column first, followed by the base column, were blander than those prepared via the reverse procedure.

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[1] **Braverman, J. B. S., and Levi, A. 1960. Comminuted Orange: A Novel Process for Its Manufacture. Food Technol. 14: 106-109.**

STUDIES ON RECOVERY OF WATER SOLUBLE ESSENCES AND DISTILLED OIL FROM ORANGE PEEL

by

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(Presented by M. K. Veldhuis)

Studies on the addition of essence to instant orange juice have indicated that more essence could be used than was available from the equivalent amount of fresh juice. The dried product is thoroughly stripped of volatile compounds during concentration and dehydration. A degree of "overflavoring" is needed to compensate for the complete loss of volatiles. Also, it was obvious that an abundance of good flavor would mask slight processing flavor acquired during concentration and drying. To have an abundance of flavor to work with, sources other than fresh juice were considered.

A simple atmospheric unit has been devised for the recovery of volatile water soluble essences and distilled orange oil from peel slurries, extracts, juices and juice components. The apparatus consisted of a turbulent-film evaporator, a stripping column, a reflux column and condenser, and a chilled product condenser and receiver. The turbulent-film evaporator permitted the use of slurries and suspensions as well as ordinary citrus juices. The distilled oil and water-soluble essences collected in the receiver and formed two layers in an oil trap. The oil layer was decanted off, leaving the aqueous layer containing the water-soluble fractions of volatile flavor and aroma components.

In a few original experiments, various products were stripped on the turbulent film evaporator and the volatile distillate was simply condensed. This material was analyzed by GLC using methylene chloride extraction to remove and concentrate the organic materials. GLC analysis of these components stripped from a slurry of ground whole orange peel at atmospheric pressure was compared to a similar analysis of a commerical juice essence. This analysis showed the same general components were present in approximately the same relative concentrations in both samples.

On a pilot scale using essence recovery equipment capable of handling from 10 to 50 gallons of feed material per hour, a number of different sources of experimental essence were studied. In most cases, the source material was ground, slurried with one or two parts of water, passed through a finisher, and the aqueous extract was used as a source for the "experimental essence." Among the sources compared were: Orange albedo, orange flavedo, ground whole orange peel, whole peeled fruit, ground whole fruit, single strength orange juice, and peel oil desludger effluent. Essences obtained from these sources were compared on a basis of chemical oxidation demand (COD), ethanol content, and total organic extractables (TOE) less ethanol. On these basis all of these materials served as good prospective sources of experimental essence. They were evaluated for flavor potency on "fold" by a 12 man taste panel. Essences of highest flavoring power were obtained from orange flavedo and from ground whole peel. Essences from ground whole peel, peeled fruit, and single strength juice all were considered to improve the quality of juice products to which they were added.

GLC analyses were carried out on essences from these sources as compared with commercial juice essence. Most of the peaks seen in commercial essence were found also in essences from ground whole peel, ground flavedo, and ground albedo. The highest amount and greatest number of components were reduced in amount. GLC analysis of the experimental essence from single strength orange juice was, for all practical purposes, identical to that from commercial orange essence. The experimental essence obtained from peel oil desludger effluents was similiar in most respects to that of commercial orange essence except that a number of the highly volatile components were missing or greatly reduced.

Using commercial peel oil desludger effluent, several experiments were carried out varying reflux ratio. The material was fed at 10 gal./hr. into the turbulent film evaporator where approximately 25 percent was vaporized and passed into the stripping column.

By controlling the temperature on the reflux condenser above the stripping column, the amount of aqueous vapors passing out the top of the stripping condenser (along with the distilled oil) was varied. The reflux ratios ranged from 2/1 to 20/1. The experimental essences were compared as before, on a basis of COD, ethanol, TOE, and TOE/°Brix of feed. They were also evaluated for "fold" and for quality as before. Generally, as the reflux ratio increased the TOE, and the TOE/°Brix feed increased. Highest fold achieved was about 1,000 in a sample which has been prepared at a reflux ratio of about 20. This sample also was judged very high in quality, both in reconstituted concentrate, and foam-mat powder. COD varied from about 2 to about 15 (x 10-^{3}), ethanol content varied from about 1 to about 7 (x 10-^{3}), TOE ranged from about 0.1 to 1.4 (x 10-^{3}), TOE/°Brix of feed ranged from about 0.078 to 1.162 (x 10-^{3}). All values except ethanol tended to go up or down as a reflux ratio increased or decreased, respectively. However, ethanol content was quite variable with some slight trend toward a decrease of ethanol as reflux ratio increased.

Regular checks of column "bottoms" indicated absence of a significant amount of either oil or essence, indicating that all volatiles passed out the top of the reflux condenser and were condensed in the chilled water condenser. The concentration of TOE in the water layer was found to depend upon the ratio of water to distilled oil. The amount of oil remained constant. Within limits, the smaller the amount of aqueous phase the smaller the total extractables in the aqueous phase. When the volume of water was limited, more of the essences dissolved in the oil, and it was apparently a question of partition.

In another series of experiments the percentage vaporization in the trubulent-film evaporator was varied from 8 to 27 percent. In each case the recovery of distilled oil was approximately 96 percent while the TOE varied only slightly. Ten percent vaporization seemed sufficient to recover most of the oil and other volatile organic material. Future experiments may reveal even smaller percentage vaporization to be adequate.

The total amount of flavoring material that can be obtained from a given amount of fruit is much larger from the peel than from the juice, but the concentration of the essence from the peel is lower because of the larger amount of oil and the partition coefficient relationship. The layer of oil can be separated and the concentration of essence continued in a rectifying column.

At present the standards of identity for frozen concentrated orange juice provides for flavor fortification with orange peel oil and essence from juice and does not include essence from peel. Peel essence has good flavoring possibilities for many purposes, however.

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UNITED STATES DEPARTMENT OF AGRICULTURE
Agricultural Research Service

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Reprints of publications may be obtained without cost
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Patents may be obtained *only* by purchase from the
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